

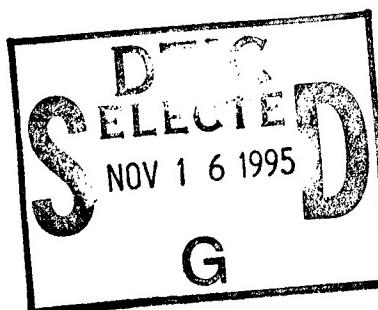
PROTECTIVE COATINGS TO PROMOTE OXIDATION RESISTANCE, WEAR RESISTANCE, AND DAMAGE TOLERANCE TO COMPOSITE STRUCTURES USING THE LTAVD PROCESS

Michael W. Dean

Vapor Technologies, Inc.
6330 Gunpark Drive
Boulder, CO 80301

January 1995

Final Report



Distribution authorized to DoD components only; Proprietary information, January 1995. Other requests for this document shall be referred to AFMC/STI.

WARNING - This document contains technical data whose export is restricted by the Arms Export Control Act (Title 22, U.S.C., Sec 2751 et seq.) or The Export Administration Act of 1979, as amended (Title 50, U.S.C., App. 2401, et seq.). Violations of these export laws are subject to severe criminal penalties. Disseminate IAW the provisions of DoD Directive 5230.25 and AFI 61-204.

DESTRUCTION NOTICE - For classified documents, follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19 or DoD 5200.1-R, Information Security Program Regulation, Chapter IX. For unclassified, limited documents, destroy by any method that will prevent disclosure of contents or reconstruction of the document.



PHILLIPS LABORATORY
Space and Missiles Technology Directorate
AIR FORCE MATERIEL COMMAND
KIRTLAND AIR FORCE BASE, NM 87117-5776

DTIC QUALITY INSPECTED 8

19951115 148

UNCLASSIFIED



AD NUMBER

AD- B205 246

NEW LIMITATION CHANGE

TO **DISTRIBUTION STATEMENT A -**
Approved for public release; Distribution unlimited.

Limitation Code: 1

FROM **DISTRIBUTION STATEMENT -**

Limitation Code:

AUTHORITY

Janet E. Mosher, Phillips Lab., Kirtland AFB, N.M.

THIS PAGE IS UNCLASSIFIED

PL-TR-95-1003

This final report was prepared by Vapor Technologies, Inc., under Contract F29601-94-C-0140 Job Order, 9991SBIR, with Phillips Laboratory, Kirtland Air Force Base, New Mexico. The Laboratory Project Officer-in-Charge was Bob Acree, (VTSC).

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely Government-related procurement, the United States Government incurs no responsibility or any obligation whatsoever. The fact that the Government may have formulated or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication, or otherwise in any manner construed, as licensing the holder, or any other person or corporation; or as conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been authored by a contractor of the United States Government. Accordingly, the United States Government retains a nonexclusive royalty-free license to publish or reproduce the material contained herein, or allow others to do so, for the United States Government purposes.

This report contains proprietary information and shall not be either released outside the government, or used, duplicated or disclosed in whole or in part for manufacture or procurement, without the written permission of the contractor. This legend shall be marked on any reproduction hereof in whole or in part.

If your address has changed, if you wish to be removed from the mailing list, or if your organization no longer employs the addressee, please notify PL/VTPT, 3550 Aberdeen Ave SE, Kirtland AFB, NM 87117-5776 to help maintain a current mailing list.

This report has been reviewed and is approved for publication.

Robert L Acree
BOB ACREE

Project Officer

FOR THE COMMANDER

L. Kevin Slimak
L. KEVIN SLIMAK
Chief, Structures and
Controls Division

Henry L Pugh Jr
HENRY L. PUGH, JR., Col, USAF
Director of Space and Missiles Technology

DO NOT RETURN COPIES OF THIS REPORT UNLESS CONTRACTUAL OBLIGATIONS
OR NOTICE ON A SPECIFIC DOCUMENT REQUIRES THAT IT BE RETURNED.

DRAFT SF 298

1. Report Date (dd-mm-yy) January 1995	2. Report Type Final	3. Dates covered (from... to) 6/94 to 1/95			
4. Title & subtitle Protective Coatings to Promote Oxidation Resistance, Wear Resistance, and Damage Tolerance to Composite Structures Using the LTAVD Process		5a. Contract or Grant # F29601-94-C-0140			
		5b. Program Element # 62601F			
6. Author(s) Michael W. Dean		5c. Project # 9991			
		5d. Task # SB			
		5e. Work Unit # 1R			
7. Performing Organization Name & Address Vapor Technologies, Inc. 6330 Gunpark Drive Boulder, CO 80301		8. Performing Organization Report # BMD094-013			
9. Sponsoring/Monitoring Agency Name & Address Phillips Laboratory 3550 Aberdeen Ave SE Kirtland AFB, NM 87117-5776		10. Monitor Acronym			
		11. Monitor Report # PL-TR-95-1003			
12. Distribution/Availability Statement Distribution authorized to DoD components only; Proprietary Information; January 1995. Other requests shall be referred to AFMC/STI.					
13. Supplementary Notes					
14. Abstract One of the major barriers that restricts the expanded use of high-performance, resin-matrix composite materials in both government and commercial applications is the lack of a reliable, cost-effective coating process. The desired technique must deposit a variety of protective coatings without degrading the underlying composite structure while minimizing any environmental hazards. This Phase I SBIR demonstrated the feasibility of using a commercially-viable coating process, called Low Temperature Arc Vapor Deposition (LTAVD), a patented variation of cathodic arc plasma deposition to apply several hard, high temperature materials on composite substrates. Three types of laminates with different surface conditions, graphite fibers, and matrix resins were used as specimens so that sample coatings for a broad range of potential composite applications were demonstrated. These results have led to expressions of possible Phase II and III support from companies in ground transportation (MASCO) and heat sinks for PWB assemblies (AMT).					
15. Subject Terms Coatings, Oxidation-resistance, LTAVD, Protective Coatings, Wear-Resistance, Arc Deposition, Vacuum Deposition, Composite Materials					
Security Classification of			19. Limitation of Abstract	20. # of Pages	21. Responsible Person (Name and Telephone #)
16. Report Unclassified	17. Abstract Unclassified	18. This Page Unclassified	Limited	28	Bob Acree (505) 846-8257

**GOVERNMENT PURPOSE LICENSE RIGHTS
(SBIR PROGRAM)**

Contract Number: F29601-94-C-0140

**Contractor: Vapor Technologies, Inc.
Boulder, CO**

For a period of four (4) years after delivery and acceptance of the last deliverable item under the above contract, this technical data shall be subject to the restrictions contained in the definition of "Limited Rights" in DFARS clause at 252.227-7013. After the four-year period, the data shall be subject to the restrictions contained in the definition of "Government Purpose License Rights" in DFARS clause at 252.227-7013. The Government assumes no liability for unauthorized use or disclosure by others. This legend shall be included on any reproduction thereof and shall be honored only as long as the data continues to meet the definition on Government purpose license rights.

Accesion For	
NTIS	CRA&I
DTIC	TAB
Unannounced	
Justification _____	
By _____	
Distribution / _____	
Availability Codes	
Dist	Avail and / or Special
E-4	

CONTENTS

<u>Section</u>	<u>Page</u>
1.0 INTRODUCTION	1
1.1 Phase I Opportunity Addressed	1
1.2 Relationship of Phase I Results to Phase II	4
1.3 Benefits of High-Performance Coatings on Composites	5
2.0 PHASE II TECHNICAL OBJECTIVE	5
3.0 PHASE I TECHNICAL RESULTS	6
3.1 LTAVD Process Description	6
3.2 Completed Coating Demonstrations	8
3.3 Justification and Rationale for Phase II	17
4.0 RECOMMENDATIONS FOR PHASE II	20

FIGURES

<u>Figure</u>	<u>Page</u>
1. Schematic of the Low Temperature Arc Vapor Deposition (LTAVD) System	7
2. Details of the internal components for the LTAVD coating process.	9
3. Zirconium Nitride (ZrN) coating (3.0 um-thick) on composite laminates.	11
4. Titanium Nitride (TiN) coating (1.6 um-thick) on composite laminates.	12
5. Copper-Chromium (CuCr) coating (1.6 um-thick) on composite laminates.	13
6. Layered (Zr/ZrN) coating (2.4 um-thick) on composite laminates	14
7. Layered (Ti/TiN) coating (6.4 um-thick) on composite laminates.	15
8. Amorphous diamond coating (0.23 um-thick) on composite laminates.	16
9. Amorphous diamond coating (0.51 um-thick) on Gr/PEEK substrate (200x).	18
10. Titanium Diboride coating (0.08 um-thick) on Gr/E substrate (200x).	18

TABLES

<u>Table</u>	<u>Page</u>
1. Technical Comparisons of Coating Technologies	3
2. Phase II Activities to Address Issues	4
3. Description of the Composite Substrates	6
4. Summary of LTAVD Coating Results	18

1.0 INTRODUCTION

One of the major barriers that restricts the expanded use of high-performance, resin-matrix composite materials in both government and commercial applications is the lack of a reliable, cost-effective coating process. The desired technique must deposit a variety of protective coatings without degrading the underlying composite structure while minimizing any environmental hazards. Requirements for resistance to oxidation, wear, and impact damage often involve conditions of extreme temperature, high contact and bearing loads, and repeated cyclic exposure to these environments. These situations demand coatings using hard, high-temperature materials that are often difficult to process.

This Phase I SBIR demonstrated the feasibility of using a commercially-viable coating process, called Low Temperature Arc Vapor Deposition (LTAVD), to apply several hard, high temperature materials on composite substrates. Three types of laminates with different surface conditions, graphite fibers, and matrix resins were used as specimens so that sample coatings for a broad range of potential composite applications were demonstrated. The promise of enabling truly fuel-efficient, non-polluting ground transportation with proprietary coatings for minimum-weight composite structures and moving mechanical parts is attractive to MASCO Corporation since they are interested in growing this market segment of their business. If the expected positive results are demonstrated in Phase II, then MASCO has indicated its possible interest in participating as a customer in a Phase III commercialization program. Further, Applied Materials Technology, Inc. is interested in using LTAVD to seal and protect prototype carbon-carbon heat sinks being developed under a Phase II SBIR, contract F33615-93-C-5348, since both the processing costs and the coating characteristics are attractive for the production volumes being projected for their anticipated Phase III effort.

The demonstration of feasibility described above has a logical extension into a Phase II coatings effort that would provide actual performance data from testing of prototype components for targeted applications, i.e. those showing the greatest potential of achieving broad-based, dual-use operational status. Also, improved design and analysis procedures for highly loaded joints and attachments in composite structures, with both fixed and moving interfaces on the component assemblies, could be verified by correlation with the test data from the proposed development effort for prototype hardware.

1.1 Phase I Opportunity Addressed

During Phase I Vapor Technologies successfully applied several high-performance coating materials to resin-matrix composite substrates using a unique, commercially-viable process called LTAVD, a patented variation of cathodic arc plasma deposition. Although some coatings on composites do exist, most techniques are limited to either one-of-a-kind aerospace applications or general-purpose industrial use by one or more of the following constraints: 1) low-volume, high-cost processes (e.g. foil wraps), 2) deficient hardness and /or temperature limits for the coating, 3) excessive thickness, poor adherence, and restricted material selection (e.g. plating), and 4) high substrate temperature (e.g. plasma spray).

LTAVD eliminates these restrictions as indicated by the following key advantages:

- 1) Difficult coatings are applied to substrates without significant surface temperature changes from ambient.
- 2) Being an enclosed, dry-vacuum coating process, LTAVD has inherent environmental safety and is compatible with production operations from the factory floor to the clean room.
- 3) It is cost effective by its ease of scale-up, efficient target utilization, high substrate packing factors, simple target forms and power supply equipment, and rapid, uniform deposition rates on parts with complex surfaces.
- 4) It offers versatility by combining high ionization energy, strong mechanical adherence, and material purity with a wide range of coating-substrate material options for both reactive and non-reactive, conformal coatings in a tailored environment with adjustable controls.
- 5) LTAVD has unique capabilities for alloying dissimilar materials in the coating, using multiple targets with independent activation energies without chemically transforming the target materials. Further elaboration of the technique involves reactive coatings, either between the ionized species and/or with partial pressure gases, such as nitrogen and oxygen, that are introduced into the chamber to form the desired thin film.
- 6) It is most productive in dense, high-purity, thin film applications, typical thicknesses range from a few hundred angstroms up to several microns.
- 7) LTAVD coatings have non-columnar structures that offer enhanced corrosion resistance and wear characteristics.

These enhancements, compared to other processes, are summarized in Table 1.

The coatings demonstrated in Phase I were Zirconium Nitride [ZrN], Titanium Nitride [TiN], Copper-Chromium [CuCr], amorphous diamond, and Titanium Diboride [TiB₂] on three types of composite substrate with epoxy, cyanate ester, and polyether-ether-ketone matrices. Each coating was inspected for surface quality, thickness, and adhesion to the substrate. Laminate coupons had a nominal size of 2.5 cm x 4.0 cm, except for the amorphous diamond and TiB₂ trials which were 1.25 cm x 3.75 cm, so that qualitative evaluations of coating uniformity could be made. These demonstrations illustrated the versatility of LTAVD since the coatings listed above represent applications ranging from large-volume commercial production (ZrN and TiN for automotive, medical, industrial, and household items) to state-of-the-art R&D activity for aerospace (TiB₂ and amorphous diamond). CuCr is representative of the multi-species class of coatings. It is a precursor to forming Cr₂O₃ protective coatings on rocket motor parts.

A technical review of the desired Indium-Tin Oxide [ITO] film properties (high optical transparency and low electrical resistivity) indicated that previous results achieved by the LTAVD process were marginal for the electro-optical applications being targeted. Further, the required refinements would eliminate the cost and production advantages of LTAVD over competing coating methods for applying ITO. Finally, since the film quality is questionable for any modified process, it was decided not to proceed with the ITO task.

Thus all of the Phase I objectives were accomplished by Vapor Technologies, Inc.:

- 1) demonstrate the feasibility of using a cost-effective, commercial coating process (LTAVD) to deposit a variety of high-performance materials in a controlled, repeatable manner,
- 2) produce sample coatings on composite substrates that are representative of the structural materials used for advanced spacecraft, aircraft, helicopters, and various ground

Table 1

TECHNICAL COMPARISONS OF COATING TECHNOLOGIES

Characteristic	LTAVD	Cathodic Arc	Sputter	Ion Plating	Evaporation	Plasma Spray	Electroplate
Coating Energy Per Ion (ev)	60 - 100	60 - 100	0.1	0.1	0.1	25-50	1
Ionization Percentage	90%	90%	30%	30%	30%	20%	N/A
Vacuum Coating	Yes	Yes	Yes	Yes	Yes	No	No
Target Use %	80%	50%	30%	50%	50%	25%	50%
Coating Structure	Non-Columnar	Non-Columnar	Columnar	Columnar	Columnar	Non-Columnar	Non-Columnar
Productivity	1	2	3	2	2	3	2
Fixturing Ease/Cost	1	2	2	3	3	3	2
Equipment & Maint. Ease/Cost	2	2	3	3	4	1	2
Versatility	1	1	1	2	2	1	3
Thermal Effect on Substrate	1	4	2	5	5	4	3

NOTE: COMPARATIVE RATINGS BASED ON 1.BEING BEST

and marine vehicles, and 3) identify commercial opportunities for transferring this technology to industrial applications that contribute to the future competitiveness of the U.S.

1.2 Relationship of Phase I Results to Phase II

From the positive Phase I results, the basis for greatly expanding the economical and innovative use of composite materials has been established. Since many proposed applications have been frustrated by the lack of the required protective coatings for the desired composite structural components, these demonstrations with the cost-effective, versatile LTAVD process offer the means for opening up the creative design opportunities for future applications that can revolutionize the engineering of highly efficient structures.

Before this promising technological breakthrough can be fully exploited, key technical and production issues that were identified during Phase I must be addressed and resolved by Phase II activities. These issues are:

- Defining operational environments for key applications, ranging from short-duration conditions on missiles (GBI) and launch vehicles to long-term operations for on-orbit spacecraft and automotive or aircraft engines.
- Selecting necessary set of coating properties (i.e. thermal, mechanical, physical, electrical, and optical) required to screen potential applications for development.
- Providing guidelines for material database requirements so that reliable design and analysis procedures address the unique features of anisotropic composites.
- Establishing chamber operating conditions that maintain high process efficiencies for complex-shaped parts and subassemblies at high packing factors.

These items are typical situations that arise in most development projects since the end users want to select the most cost-effective coating that satisfies their requirements. However, delivered cost is a function of not only the material used and the part geometry but also the process time and the chamber setup required to deposit the specified coating. None of the above issues are exceptional and are readily resolved by the actions and activities planned for Phase II, as described in Table 2:

Table 2. Phase II Activities to Address Issues.

Issue	Phase II Activity
1) Application requirements	<ul style="list-style-type: none">• Identify range of possible dual-use applications• Use selection criteria to prioritize areas with best potential• Develop specifications from industry inputs for selected items
2) Coating properties for screening	<ul style="list-style-type: none">• Select set of discriminators based on decision criteria from (1)• Adjust property set for schedule/budget constraints on testing

3) Material database guidelines	<ul style="list-style-type: none"> • Identify unique needs for material performance data and testing: <ul style="list-style-type: none"> - component integrity for coating thickness versus loading condition (temperature, contact and bearing stress levels, time) - wear or oxidation rates versus coating thickness, load levels, and surface-ply material forms (unidirectional tape vs fabric) • Document results in an Applications Design Guide
4) Processing efficiency	<ul style="list-style-type: none"> • Establish optimum process conditions for selected applications: <ul style="list-style-type: none"> - ionizing current levels and magnetic field strengths - support fixturing and ease of loading/unloading - substrate offset distances, bias voltage, and cleaning method • Document predicted production costs

1.3 Benefits of High-Performance Coatings on Composites

The results of this Phase I SBIR have demonstrated the feasibility of using a cost-effective, commercially-viable coating process (LTAVD) to deposit high-performance materials on resin-matrix composites. This will enable innovative thermomechanical applications as well as extend the range of structural uses for composites that have previously been considered unattainable due to the cost of the coating processes, restricted material choices, and/or a lack of operational heritage and engineering design experience, e.g. on-orbit performance of space structures.

2.0 PHASE II TECHNICAL OBJECTIVES

The central goal of the Phase II program is to evaluate new applications for composite components that use LTAVD coatings with the high performance materials demonstrated in Phase I. Initial efforts will focus on the transportation and electronics areas previously identified. Critical DoD applications related to protective coatings for space structures, propulsion systems, launch vehicle shrouds, and high temperature, erosion surfaces will also be addressed. Each item must be scrutinized by a cost/benefit analysis that indicates the performance gained and the weight removed for what amount of incremental cost. The key to each successful implementation is the use of reliable coatings demonstrated in Phase I and deposited by the versatile, cost-effective LTAVD process. The specific objectives to be achieved during Phase II are listed below:

1. Develop screening criteria to identify the most promising applications.
2. Define component performance specifications for selected applications.
3. Fabricate and Test prototype composite components.
4. Characterize coatings for properties critical to application screening.
5. Generate material database guidelines that support reliable design procedures for applications using coated composite components.

3.0 PHASE I TECHNICAL RESULTS

The Phase I tasks demonstrated the feasibility of using the LTAVD process to deposit several protective coatings on three composite substrates. These laminates, described in Table 3, were selected to cover the range of surface conditions, graphite fibers (Gr), and matrix resins that are typical of many potential composite applications. Thus all of the Phase I objectives were accomplished by Vapor Technologies, Inc.: 1) demonstrate the feasibility of using a cost-effective, commercial coating process (LTAVD) to deposit a variety of high-performance materials in a controlled, repeatable manner, 2) produce sample coatings on composite substrates that are representative of the structural materials selected for advanced spacecraft, aircraft, helicopters, and various ground and marine vehicles, and 3) identify commercial opportunities for transferring this technology to industrial applications that contribute to the future competitiveness of the U.S.

Table 3. Description of the Composite Substrates.

Laminate	Graphite Fiber	Resin Matrix	Thickness (mm)	Surface Condition
1) Fabric, 5HS weave, one ply	AS4	934 Epoxy (E)	0.406	Smooth with depressions at yarn crossovers
2) Unidirectional tape, 0/±45/90	P75	954-3 Cyanate Ester (CE)	1.016	Satin texture from peel ply
3) Fabric, 8 HS comingled yarn	T300	Polyether-ether ketone (PEEK)	0.762	Upper-pressure bag pattern Lower-caul plate smooth

As discussed above, one of the important steps in any coating demonstration was the definition of the optimum process conditions for the composite substrates, i.e. cleaning method, offset distance, fixturing, and current and voltage settings. These items are described in the following section that presents an overview of the LTAVD process.

3.1 LTAVD Process Description

The LTAVD system and setup is schematically illustrated in Figure 1. The major parts of this system are the vacuum chamber (1) and control cabinet, the target material or cathode (2) where the ionizing arc is ignited, the substrates (3 and 4) to be coated which may be placed all around the chamber as well as along its entire length, and the vacuum pumping system (5 through 11). Although the vacuum chamber may have any shape, its impact on the target to substrate distance, i.e. the offset distance between (2) and (3), is often a critical factor since it affects the deposition rate, substrate surface temperature, and the coating uniformity.

Surface preparation is another essential part of any successful coating process since the time and cost of this step can affect the process production efficiency as well as the coating quality. VT has a complete cleaning facility, including capabilities for vapor

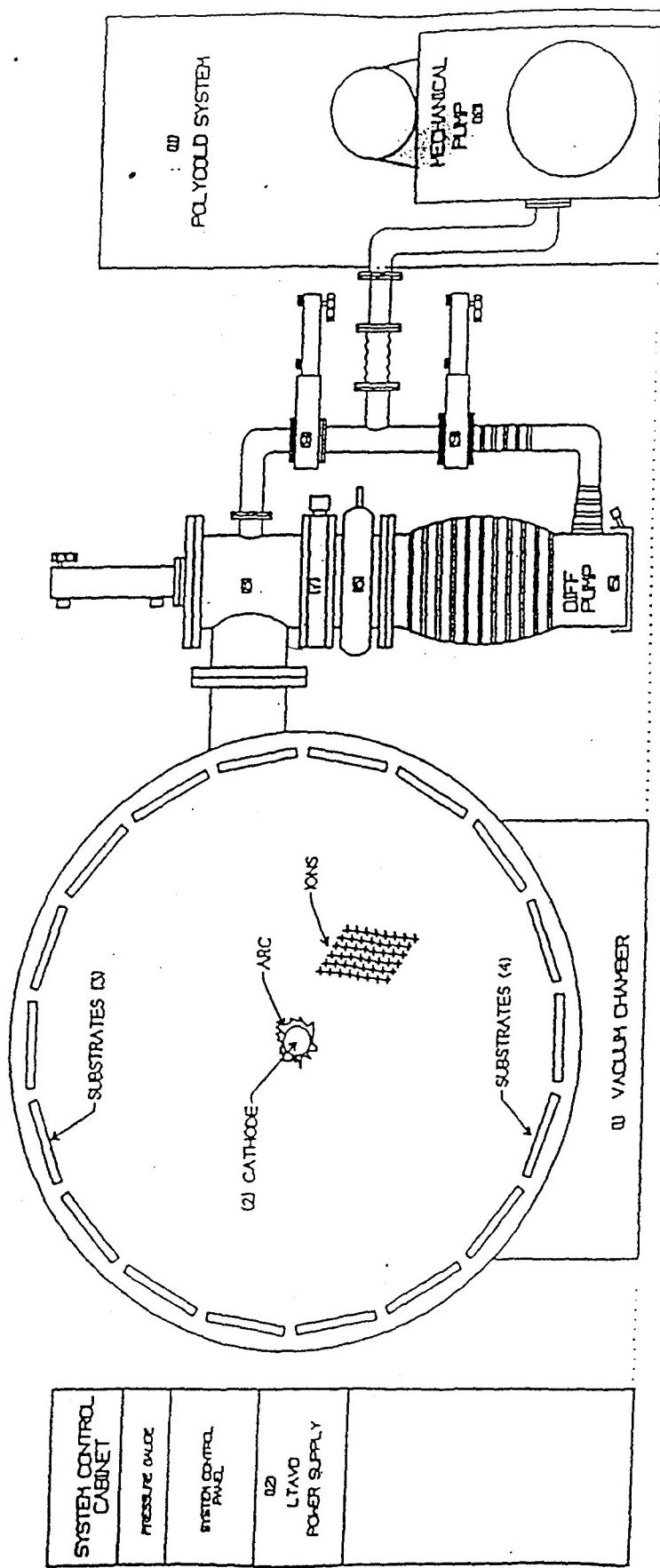


Figure 1. Schematic of the Low Temperature Arc Vapor Deposition (LTAVD) System.

degreasing, aqueous degreasing, ultrasonic rinses with hot and cold deionized water, hot-air drying with an air knife, plasma etching, and a technique for in-chamber sputter etching with Argon gas. The Phase I efforts focused on the use of etching procedures for cleaning substrates that avoided aqueous solutions or hazardous chemicals. These approaches are also quicker and eliminate conflicts with end-user requirements such as water absorption on composite space structures. Both etching techniques were found to be compatible with all three of the composite substrates and resulted in reliable coatings, as discussed in the following section.

The component details of the LTAVD coating process are shown in Figure 2. Items (1) through (9) inside the vacuum chamber (not shown) are labeled. The process starts with an electric arc (5) being ignited by the arc striker (7) and the anode (6) on the surface of the target cathode (1). The arc is repeatedly guided up, down, and around the length of the target, creating a flash evaporation of highly energetic ions. This plasma uniformly disperses throughout the vacuum chamber, forming a dense, adherent film on the substrate (9) which may be electrically biased. If a gas is now introduced into the chamber, the ions will combine with the disassociated gas to form a reacted coating. An example of this technique is the formation of titanium nitride on a substrate, using a titanium target with nitrogen gas present. Since the targets typically are cylindrical rods, this enhances two of LTAVD's significant commercial advantages: 1) high parts coating throughput due to the 360-degree process zone, and 2) high target utilization rates of 90% or more, compared to other processes such as sputtering with about 30%. Further, most vacuum deposition processes take place in the 10^{-8} Torr range for direct coatings while reactive depositions are at 10^{-2} Torr or lower pressures. Both pressure extremes are accommodated by LTAVD. Finally, this process can use multiple targets either to achieve higher rates of deposition or to co-deposit alloy coatings augmented by inexpensive fixtures that range from static racks with clips to rotating planetary mechanisms if necessary. Having described the key features of the coating system and established the versatile capabilities of the LTAVD process, the next section reviews the coating demonstrations performed on composite substrates during Phase I.

3.2 Completed Coating Demonstrations

The initial coating trial was conducted as part of Task 1 to identify the LTAVD process conditions that were compatible with composite substrates. A thin film ($1.0 \mu\text{m}$ thick) of Zirconium Nitride [ZrN] was deposited on the Gr/E laminate. Thickness was measured with a DEKTAK 3030. This exercise indicated that ambient surface temperatures were maintained on the substrates during the coating operation for offset distances of atleast 20 cm. However, less offset distance can be compensated for by reducing the power setting and/or using rotating fixtures. Dense, adherent ZrN coatings were made on the substrate whether vapor and aqueous degreasing or plasma and sputter etching methods of cleaning were used. Therefore, the etching techniques are recommended since these methods tend to be quicker, introduce few, if any, contaminants, and avoid the use of hazardous chemicals. All coating trials passed the tape pull test, indicating good adhesion to the substrates since no coating separated from the composite surfaces at the material interface.

1. CATHODE (TARGET)
2. ANODE ASSEMBLY
3. TARGET HOLDER
4. ARC GUIDANCE/CONTROL SYSTEM
5. ARC STRIKER ASSEMBLY
6. ARC STABILIZER
7. DC CURRENT POWER SUPPLY
8. DC CURRENT POWER SUPPLY
9. SUBSTRATE

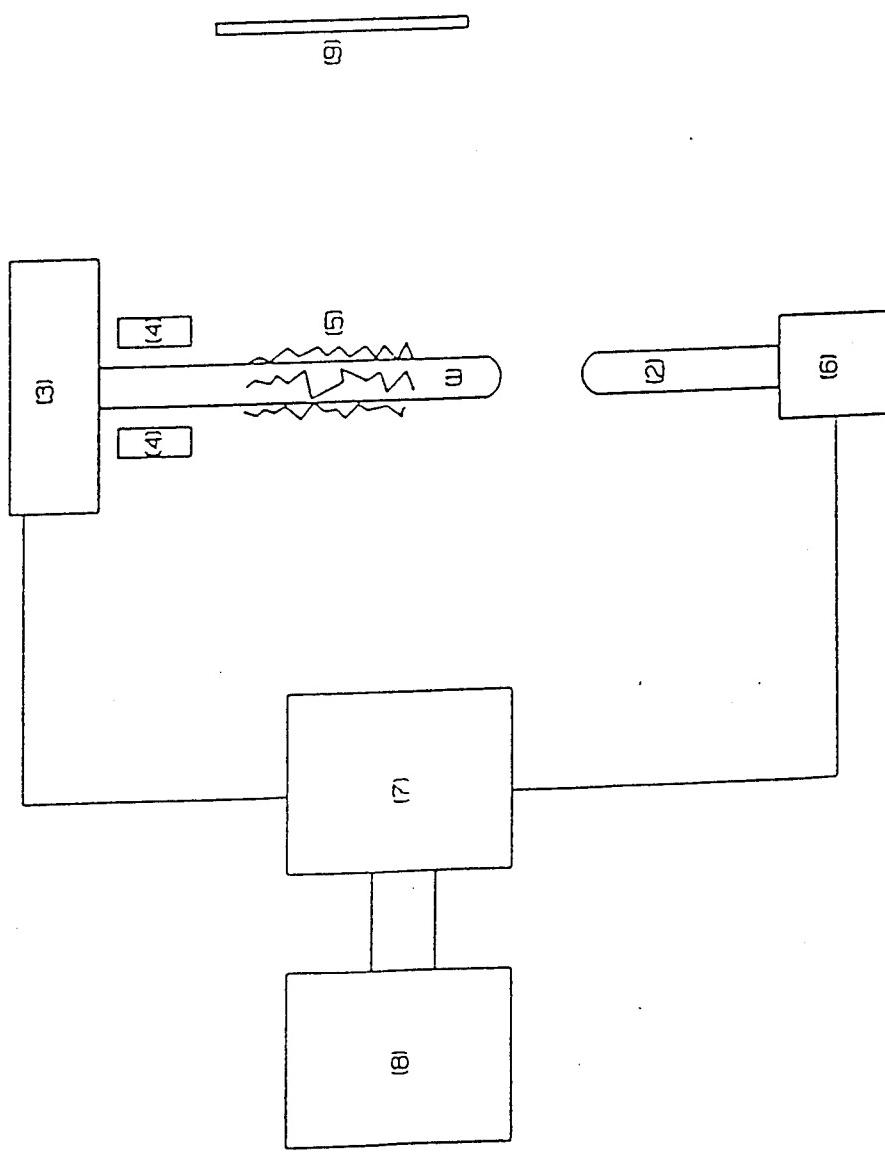


Figure 2. Details of the internal components for the LTAVD coating process.

Once the optimum processing conditions were identified, a production coating run, depositing 3.0 μm of ZrN on all three composite substrates (Figure 3), was done for Task 2. This used a rotating fixture to demonstrate uniform material distribution on all surfaces of a part. In Task 3 a 1.6 μm -thick coating of TiN was deposited on the Epoxy and PEEK substrates (Figure 4). Both Nitrides have melting temperatures of about 3000°C but oxidize in air at 1100°C to 1200°C. Their hardness is 8 to 9 on the Mohs scale and they are commercially used for wear- and corrosion-resistant applications.

The third coating demonstration (Task 4) co-deposited 1.6 microns of Copper-Chromium [CuCr] on all three composite substrates (Figure 5). Being statically mounted on the vacuum chamber inner wall, the substrates were coated with CuCr on only one surface of the laminate during processing. Both the distance (30 to 35 cm) from the target and the relative ease of vaporizing CuCr minimized any rise in the substrate surface temperature, resulting in a uniform appearance on the coated surfaces. The microstructure is an intimate mixture of Cr particles in a Cu-rich matrix with occasional round Cr-rich microdroplets. CuCr coatings are a precursor to forming a Cr_2O_3 surface, an excellent oxidation barrier melting at 2270°C. It is currently used to protect rocket motor parts.

It was originally planned to demonstrate an Indium-Tin Oxide (ITO) coating at this stage of the project. However, a technical review of the desired ITO film properties (high optical transparency and low electrical resistivity) indicated that previous results achieved by the LTAVD process were marginal for the electro-optical applications being targeted. The required refinements would eliminate the cost and production advantages of LTAVD over competing coating methods for applying ITO. Plus, the film quality was questionable for the modified process. Therefore, the ITO task was stopped and the effort focused on applying amorphous diamond and Titanium Diboride [TiB_2] coatings to the substrates.

As the amorphous diamond and TiB_2 demonstrations were about to begin, a failure in the cooling lines shut down the R&D vacuum chamber with the proprietary duct configuration required for these advanced materials. While the chamber interior and the complex ducting were cleaned and dried before attempting to restart the R&D chamber, layered Zr/ZrN and Ti/TiN coatings (Task 5) were applied to the composite substrates. The layering begins with a thin, all-metal interface being applied to the substrate followed by the ZrN or TiN. This sequence is repeated until the desired thickness is achieved. Previous experience on other substrates has indicated that layered coatings are more durable since the more compliant metallic interface allows the relatively brittle Nitrides to adjust to larger temperature changes and/or mechanical strains without cracking, particularly when thicker coatings are required. The coating thickness was 2.4 microns for the Zr/ZrN samples (Figure 6) and 6.4 microns for the Ti/TiN samples (Figure 7). The Ti/TiN coatings had a pattern of ridges on the surface. These Ti-accumulations appear to be from migrating species in the layered coating, suggesting that the thicker coatings may require some modifications to the process conditions for smooth, outer surfaces.

Restarting the R&D vacuum chamber took much longer than expected, but the coating demonstrations for amorphous diamond and TiB_2 were done during mid-January,



(a) Graphite/Epoxy substrate (250x).



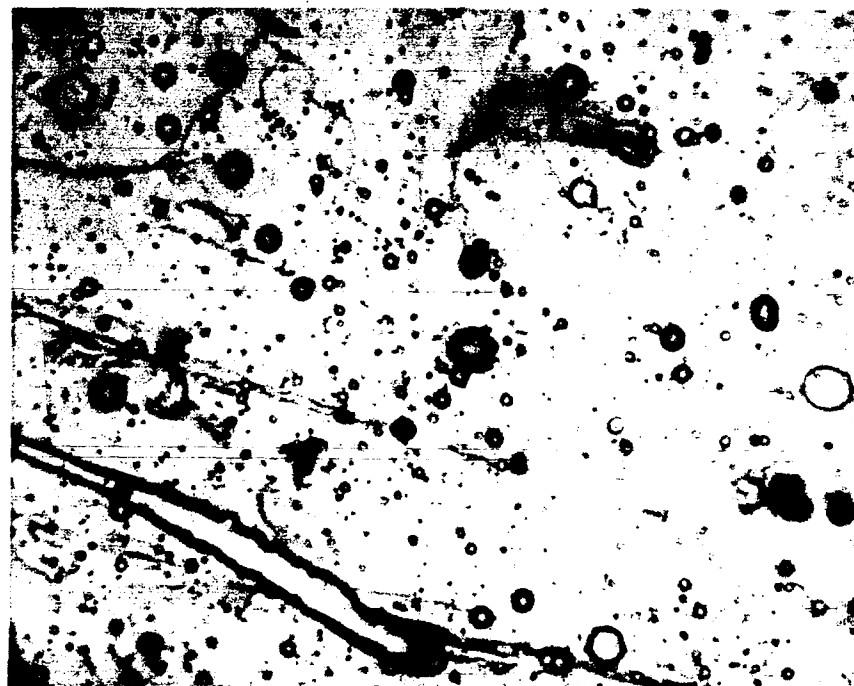
(b) Graphite/Cyanate Ester substrate (200x).

(c) Graphite/PEEK substrate (200x).

Figure 3. Zirconium Nitride [ZrN] coating (3.0 μm -thick) on composite laminates.

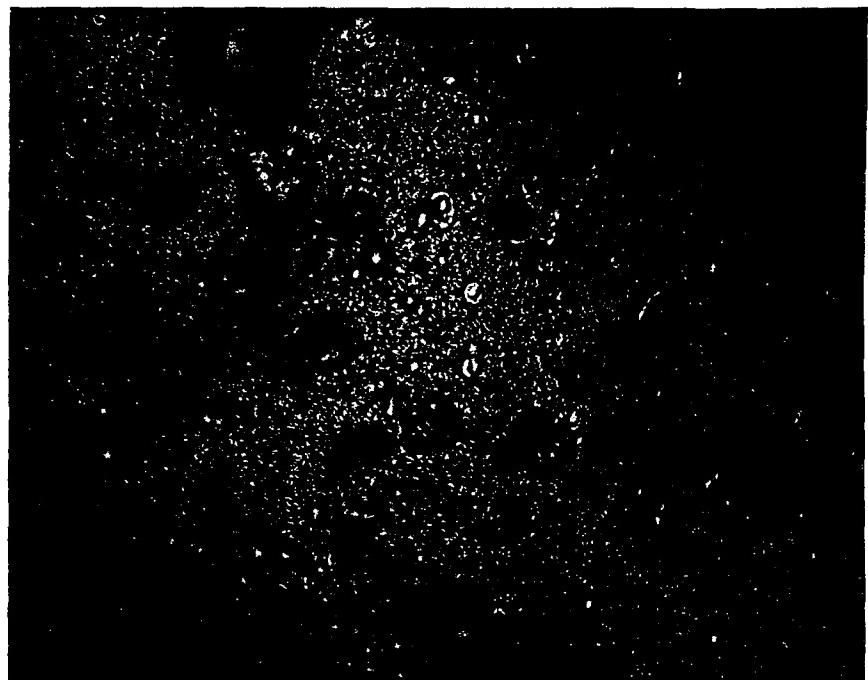


(a) Graphite/Epoxy substrate (250x).

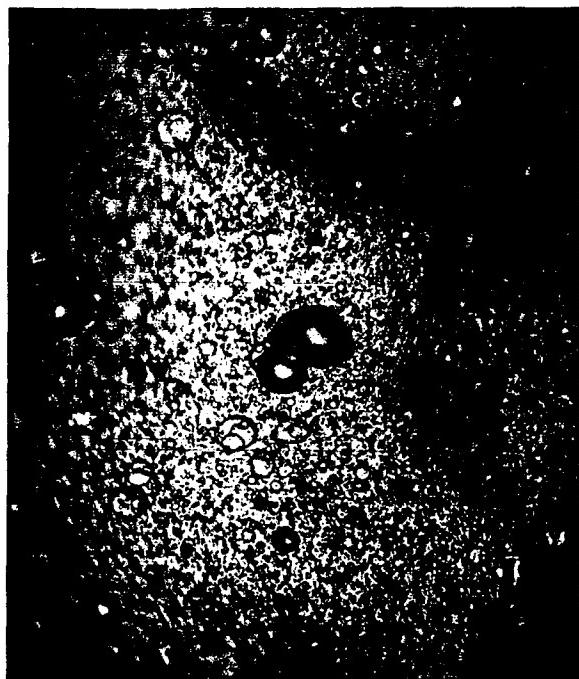


(b) Graphite/PEEK substrate (266x).

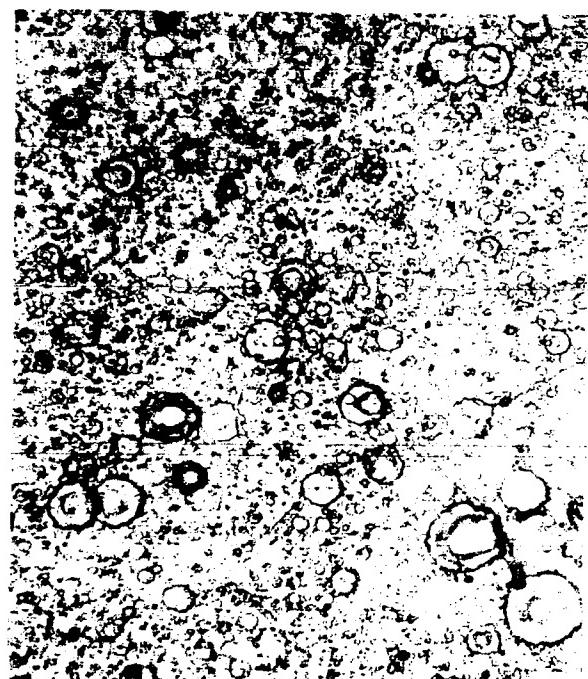
Figure 4. Titanium Nitride [TiN] coating (1.6 μm -thick) on composite laminates.



(a) Graphite/Epoxy substrate (200x).

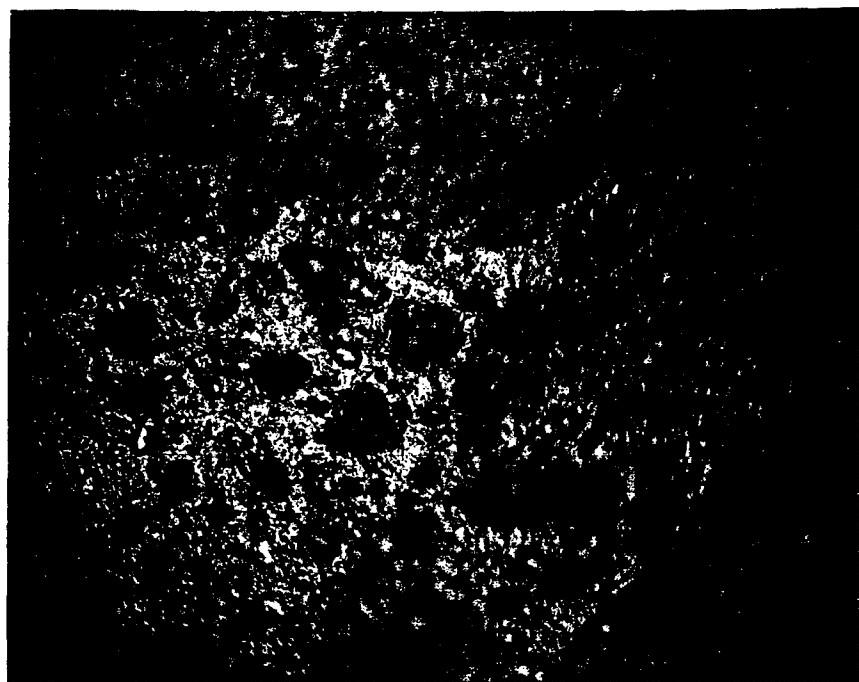


(b) Graphite/Cyanate Ester substrate (200x).

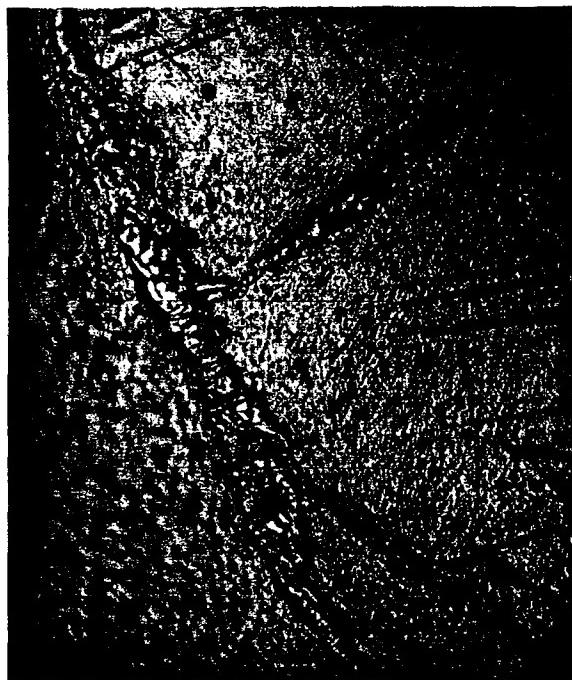


(c) Graphite/PEEK substrate (400x).

Figure 5. Copper-Chromium [CuCr] coating (1.6 μm -thick) on composite laminates.



(a) Graphite/Epoxy substrate (200x).



(b) Graphite/Cyanate Ester substrate (200x).



(c) Graphite/PEEK substrate (200x).

Figure 6. Layered $[Zr/ZrN]_3$ coating (2.4 μm -thick) on composite laminates.



(a) Graphite/Epoxy substrate (200x).



(b) Graphite/Cyanate Ester substrate (200x).

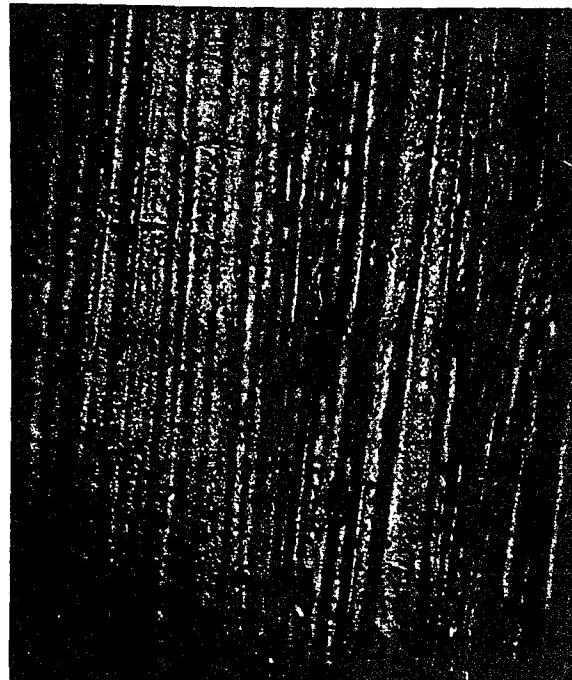


(c) Graphite/PEEK substrate (200x).

Figure 7. Layered $[Ti/TiN]_3$ coating (6.4 μm -thick) on composite laminates.



(a) Graphite/Epoxy substrate (200x).



(b) Graphite/Cyanate Ester substrate (200x).



(c) Graphite/PEEK substrate (200x).

Figure 8. Amorphous diamond coating ($0.23\text{ }\mu\text{m}$ -thick) on composite laminates.

1995. The initial amorphous diamond specimens shown in Figure 8 had a coating thickness of 0.23 μm and were cleaned by plasma etch. A second Gr/PEEK sample shown in Figure 9 was cleaned by the in-chamber sputter etch method and received a 0.5 μm -thick coating. All of these amorphous diamond coatings exhibited the following features: 1) a characteristic oil-sheen coloration and appearance due to optical refraction, and 2) the presence of cracks in the coating to relieve high internal stresses. This cracking was reduced for the thin Gr/E substrate since the stiff amorphous diamond material caused the specimen to curl up in response to the internal stresses in the coating. The CE and PEEK substrates were thick enough to resist this bending effect. Despite the cracking the coated regions showed good adhesion to the substrates. Additional Phase II development to identify the processing conditions that eliminate this cracking is required if VT is to offer a production capability for amorphous diamond coatings on composites.

The initial TiB_2 coating (0.08 μm -thick) was completed on a Gr/E substrate (Figure 10). However, further work was not possible when the target cracked after several minutes into the next coating run. A preliminary investigation indicated that this failure was the result of thermal stresses in the TiB_2 target caused by local heating in the target fixture that had been designed for carbon targets that deposit amorphous diamond. Apparently the thermal and electrical properties of TiB_2 are such that the carbon target fixture must be modified to work with another material in the LTAVD process. Again, further Phase II effort is necessary if VT is to offer a production capability for Titanium Diboride [TiB_2] coatings on composites.

With the completion of these last two coating efforts, all of the Phase I objectives were accomplished by Vapor Technologies, Inc.: 1) demonstrate the feasibility of using a cost-effective, commercial coating process (LTAVD) to deposit a variety of high-performance materials in a controlled, repeatable manner, 2) produce sample coatings on composite substrates that are representative of the structural materials used for advanced spacecraft, aircraft, helicopters, and various ground and marine vehicles, and 3) identify commercial opportunities for transferring this technology to industrial applications that contribute to the future competitiveness of the U.S.

3.3 Justification and Rationale for Phase II

During Phase I Vapor Technologies, Inc. demonstrated the feasibility of depositing seven high-performance coatings on three types of graphite fiber/resin matrix composite materials with the commercially-viable coating process, called Low Temperature Arc Vapor Deposition (LTAVD). These coatings are typical of the difficult-to-process, high-temperature materials required for protecting high-performance structures that operate in severe environments, whether terrestrial, atmospheric, or out in space. These results are summarized in Table 4.

Table 4. Summary of LTAVD Coating Results.

Task	Coating	Thickness (μm)	Tape pull	Substrate photos (Fig. #)			Comments
				E	CE	PEEK	
		Dektak 3030					
1,2	Zirconium Nitride [ZrN]	1.0, 3.0	pass	3a	3b	3c	Rotating fixture, lower energy levels
3	Titanium Nitride [TiN]	1.6	pass	4a	n/a	4b	Plasma etch clean- ing for composites
4	Copper- Chromium [CuCr]	1.6	pass	5a	5b	5c	Co-deposit two metals, same target
5	Layered 3x[Zr/ZrN]	2.4	pass	6a	6b	6c	More compliant interface than (2)
5	Layered 3x[Ti/TiN]	6.4	pass	7a	7b	7c	Compliant interface Ti accumulations
6	Amorphous Diamond	0.23 0.51	pass pass	8a n/a	8b n/a	8c 9	1st trial conditions, Sputter etch
6	Titanium Diboride [TiB ₂]	0.08	pass	10	n/a	n/a	Initial trial stopped, cracked target

Note: 10,000 angstroms equals 1.0 micron (μm).



Figure 9. Amorphous diamond coating
(0.51 μm -thick) on Gr/PEEK
substrate (200x).

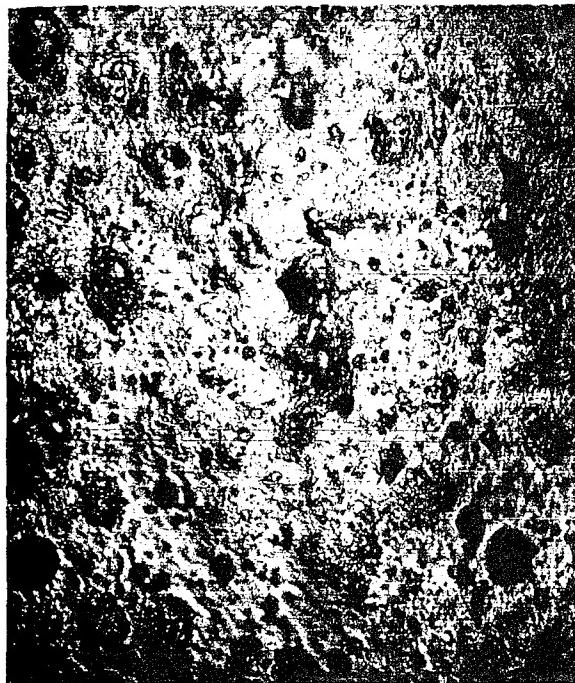


Figure 10. Titanium Diboride coating
(0.08 μm -thick) on Gr/E
substrate (200x).

From these novel efforts the following technical knowledge and issues were identified:

1) LTAVD process conditions are easily modified for coating composites.

Using the many process variables, such as current levels, magnetic field strengths, fixturing, offset distances, bias voltage, and cleaning methods, it was a straight-forward exercise to find the optimum settings that maximized part throughput while maintaining ambient surface temperatures on the composite substrates. In particular, the discovery that quick, non-hazardous etching procedures could be used for cleaning laminate surfaces was a significant factor in determining that efficient production would also result in dense, adherent coatings on composite materials.

2) Cost-effective LTAVD coatings encourage commercial uses of composites.

Two major commercial applications for composites with LTAVD coatings were identified during Phase I. First, composite structures and parts for ground transportation are attractive future market segments for MASCO Corporation. And secondly, Applied Materials Technology, Inc. wants to seal and protect carbon-carbon heat sinks for electronics applications being developed under a Phase II SBIR, contract F33615-93-C-5348. Both the processing costs and the coating characteristics of LTAVD are attractive for the production volumes being projected for their anticipated Phase III effort.

3) Requirements for specific thermomechanical structural uses must be identified.

The range of possible applications for composites with novel coatings is very broad and the critical need is to impose a rational selection procedure that will focus future development efforts on the most promising opportunities. An important criteria is the likelihood of commercial implementation and the best indicator of this is the potential commitments made by industry to extend their support of the Phase I feasibility demonstrations in potential Phase II and III efforts, such as the MASCO and AMT interests identified by VT.

4) Necessary data to screen advanced applications is ill-defined.

There are major gaps in current testing methods to characterize not only the performance of composite materials but also the enhancements provided by coatings on composites. Since the potential uses specify performance properties in all types of environments (i.e. thermal, mechanical, physical, electrical, and optical), developing an adequate database of material properties is prohibitive in terms of both the time and the cost without some screening criteria to focus these development efforts.

5) LTAVD production efficiency must be shown for specific part geometries.

Although VT has demonstrated the versatility of the LTAVD process, the actual cost-effectiveness is dependent on the size, shape, location of the surfaces to be coated, and

throughput required for a particular part. This is an essential Phase II effort if the novel technology is to be successfully commercialized.

4.0 RECOMMENDATIONS FOR PHASE II

A brief overview of the Phase II program is provided by the following list of major tasks. VT proposes these five steps as the most direct way of successfully demonstrating that cost-effective, high-performance coatings will enable a commercially-viable structural technology for new applications of government-funded research. These tasks are:

- 1) Identification:** Develop screening criteria to identify the most promising applications with significant dual-use potential. This is the crucial step since there exists such a wide range of operational environments, ranging from short-duration conditions on missiles (GBI) and launch vehicles to long-term situations for spacecraft and automotive or aircraft engines.
- 2) Selection:** Define the component performance specifications for the selected applications and identify those material properties essential to the screening procedure so that the necessary characterization of coatings on composite structures and thermomechanical parts can be performed.
- 3) Development:** Fabricate and test prototype composite components to verify part performance and to establish LTAVD operating conditions for optimal process efficiencies with complex-shaped parts and subassemblies at high packing factors.
- 4) Documentation:** Generate the material database guidelines that support reliable design procedures for applications using coated composite components and publish the results that correlate the design and analysis methods with the test data.
- 5) Private Sector Transition Plan:** Based on the Phase II results formulate the Phase III Product Commercialization Plan and recruit industrial partners to participate in the Phase III program. Key aspects of the Plan will be:
 - a) Market segment analysis.
 - b) Pricing strategies for end-products and manufacturing.
 - c) Production plans for optimizing LTAVD in these new markets.
 - d) Transition mechanisms for general industrial use of LTAVD and the new products being offered.

DISTRIBUTION LIST

AUL/LSE Bldg 1405 - 600 Chennault Circle Maxwell AFB, AL 36112-6424	1 cy
DTIC/OCC Cameron Station Alexandria, VA 22304-6145	2 cys
AFSAA/SAI 1580 Air Force Pentagon Washington, DC 20330-1580	1 cy
PL/SUL Kirtland AFB, NM 87117-5776	2 cys
PL/HO Kirtland AFB, NM 87117-5776	1 cy
Official Record Copy	
PL/VTSC/Bob Acree	2 cys
Dr. R. V. Wick PL/VT Kirtland, AFB, NM 87117-5776	1 cy